Supporting Information for

Catalytic Alcoholysis of Tetramethylsilane *via* Pt-Mediated C–H Bond Activation

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General considerations. All complexes and manipulations were carried out in the inert atmosphere provided by standard Schlenk and vacuum line techniques or by a nitrogen-filled glove box. Solvents for synthesis were dried by passage over a column of activated alumina and deoxygenated by sparging with dry nitrogen. 2,2,2-Trifluoroethanol-d_3 (TFE-d_3, Cambridge) was dried with 3 Å mol sieves, which had been pretreated with acetone-d_6 and activated at 150 °C under dynamic vacuum, and vacuum distilled. THF-d_8 (Cambridge) was stored under static vacuum over purple sodium benzophenone ketyl. Methylene chloride-d_2 (Cambridge), tetramethylsilane (Aldrich), Li(CH_2SiMe_3) (Aldrich) and tris(pentafluorophenyl)borane (Strem) were used as received without further purification. The reagents $PtCl_2(SMe_2)_2$,[1] (NN)$PtMe_2$ (**1**),[2] and $H(OEt_2)_2[B(C_6F_5)_4]$[3] were prepared by literature procedures.

NMR spectra were recorded on Varian Mercury 300 (^{1}H, 299.8 MHz; ^{13}C, 75.4 MHz), Varian Inova 500 (^{1}H, 499.8 MHz) and Varian Inova 600 (^{1}H, 599.8 MHz) spectrometers. ^{1}H and ^{13}C NMR spectra were referenced to TMS using the residual ^{1}H and ^{13}C impurities of the given solvent. All chemical shifts are reported using the standard δ notation in parts-per-million; positive chemical shifts are to a higher frequency from TMS. IR spectra were recorded in a 10-cm path length gas cell on a BioRad FTS 3000 spectrophotometer. All platinum compounds gave satisfactory analyses, which were performed at Midwest Microlab, LLC.

Reaction of [(NN)PtMe(TFE-d_3)]$^+$ (2) with TMS. In a typical reaction, **1** (5 mg, 0.01 mmol, 1 equiv) and $B(C_6F_5)_3$ (25 mg, 0.05 mmol, 5 equiv) were combined in an oven-dried NMR tube equipped with a re-sealable Teflon valve. 2,2,2-Trifluoroethanol-d_3 (0.6 ml) was added to the tube by syringe and the valve was closed. Within a few minutes the red platinum complex dissolved, with reaction, to give an orange solution of **2**. This solution was then degassed by three freeze-pump-thaw cycles. TMS (0.35 mmol, 35 equiv) was added to the NMR tube from a calibrated gas bulb to give a solution with [TMS] = 0.52 M. The reaction mixture was maintained at 25 °C in the probe of an NMR spectrometer and the reaction progress was monitored by ^{1}H NMR spectroscopy for 18 hr, during which time the resonance for TMS (δ 0.0 ppm) decayed with concomitant growth of the resonance for $(CH_3)_3SiOCD_2CF_3$ (δ 0.18 ppm); at late reaction times (>70% conversion) a resonance at δ 0.23 ppm, attributed to $(CH_3)_2Si(OCD_2CF_3)_2$, began to grow in slowly. After 18 hr (80% conversion based on TMS), the sample was frozen and 0.29 mmol non-condensable gas (29 equiv) was collected by Toepler pumping and analyzed by gas-phase IR spectroscopy (C–H bending region of the IR spectrum: 1302 (CH_4), 1157 (CH_3D), 1090 (CH_2D_2) and 1034 (CHD_3) cm^{-1}). ^{13}C NMR analysis after Toepler pumping showed new resonances for the silyl products (δ / ppm): –3.66 ($^1J_{SiC}$ = 37 Hz,

$Si(CH_3)_2$); –0.70 ($^1J_{SiC}$ = 30 Hz, $Si(CH_3)_3$); 125.6 ($^1J_{FC}$ = 277 Hz, $Si(OCD_2CF_3)_2$); 126.1 ($^1J_{FC}$ = 277 Hz, $Si(OCD_2CF_3)$). Resonances for the methylene carbons of the silyl products could not be resolved from the TFE-d_3 methylene resonance.

Preparation of (NN)Pt(CH_2SiMe_3)$_2$ (3). An oven-dried 250 ml round-bottomed flask was charged with $PtCl_2(SMe_2)_2$ (1.01 g, 2.59 mmol, 1 equiv) under an atmosphere of Argon. Dry, degassed diethyl ether (100 ml) was added by cannula transfer and the resulting mixture was cooled in a dry ice/acetone slush. Solid $Li(CH_2SiMe_3)$ (0.515 g, 5.47 mmol, 2.11 equiv) was added to the cold suspension and the mixture was stirred for 90 minutes before being warmed in an ice water bath. After an hour at 0 °C, the ice water bath was removed and the reaction mixture was warmed to room temperature; CH_2Br_2 (1 ml) was added to the reaction mixture to quench any excess $Li(CH_2SiMe_3)$. Addition of the α-diimine, 1,2-bis(3,5-dimethylphenylimino)butane (0.787 g, 2.69 mmol, 1.04 equiv), resulted in a color change to give an intense purple solution. After 2 hr, the entire volume of ether was stripped off by vacuum distillation. The dark residue was extracted with dry, degassed petroleum ether (ca. 150 ml); the solution was filtered and concentrated to 50 ml *in vacuo* then cooled to –35 °C overnight. A dark purple, semi-crystalline solid was deposited, collected by filtration and dried *in vacuo* (yield, 1.01 g). The supernatant solution was concentrated to 10 ml and cooled to –35 °C overnight to deposit a second crop of product (0.40 g) for an overall yield of 83%. Anal. Calcd for $C_{28}H_{46}N_2PtSi_2$: C, 50.81; H, 7.00; N, 4.23. Found: C, 51.32; H, 7.66; N, 4.08. ^{1}H NMR (300 Mhz, CD_2Cl_2) δ / ppm: –0.26 (s, –$Si(CH_3)_3$, 18H); 1.08 (s, Pt–CH_2, $^2J_{PtH}$ = 97 Hz, 4H); 1.21 (s, N=C–CH_3, 6H); 2.38 (s, Ar–CH_3, 12H); 6.64 (s, *o*-Ar*H*, 4H); 6.93 (s, *p*-Ar*H*, 2H).

Protonolysis reactions of 3. In a typical reaction, an oven-dried NMR tube equipped with a re-sealable Teflon valve was charged with **3** (5 mg, 0.008 mmol, 1 equiv) and $H(OEt_2)_2[B(C_6F_5)_4]$ (12 mg, 0.12 mmol, 1.5 equiv). THF-d_8 (ca. 0.6 ml) and 2,2,2-trifluoroethanol-d_3 (0.62 mmol, 78 equiv, 1 M) were condensed into the tube with liquid nitrogen and kept frozen until immediately before insertion into the NMR probe. The reaction solution was thawed in a dry ice/acetone slush, shaken (to dissolve solids) and inserted into the NMR spectrometer, which was pre-cooled to –80 °C. A ^{1}H NMR spectrum was collected immediately and showed quantitative formation of **2** and two equivalents of $(CH_3)_3SiOCD_2CF_3$. ^{1}H NMR (500 MHz, THF-d_8) δ / ppm: 0.11 (s, –$Si(CH_3)_3$, 18H); 0.57 (s, Pt–CH_2D, 2H); 1.93 (s, N=C–CH_3, 3H) 2.08 (s, N=C–CH_3, 3H); 2.32 (s, Ar–CH_3, 6H); 2.34 (s, Ar–CH_3, 6H); 6.58 (s, *o*-Ar*H*, 2H); 6.80 (s, *o*-Ar*H*, 2H); 7.04 (s, *p*-Ar*H*, 1H) ; 7.07 (s, *p*-Ar*H*, 1H).

References

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